COPOLYMER COMPOSITION STUDIES

BY

ROLAND ERIC FLORIN

B. S., University of Illinois, 1936

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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Copolymerizations in emulsion and in benzene solution were compared for the co-monomers styrene (M_1) and methyl methacrylate (M_2).

Composition data were obtained using monomer ratios of 3.847, 1.040 and 0.2402, for the two processes at 35°. The standard recipe for emulsion was 60 g. monomers, 105 g. 3 per cent soap solution (P. and G. SF Flakes), 10 ml. 3 per cent potassium persulfate solution, and 0.21 g. dodecyl mercaptan. For solution operation, the recipe was 60 g. monomers, 50 g. benzene, and 1.000 g. benzoyl peroxide. Both types of polymer were isolated by reprecipitation from benzene solution with methanol, and evaporation of frozen benzene solutions as described by Mayo and Lewis (1).

The parameters of the copolymerization equation (2) were evaluated from conversion and carbon analysis data, by a graphical method similar to that of Wall, Powers, Sands and Stent (3). These parameters were found to be: for solution, $r_1 = 0.50 \pm 0.02$, $r_2 = 0.44 \pm 0.02$; for emulsion, $r'_1 = 0.56 \pm 0.02$, $r'_2 = 0.49 \pm 0.02$.

These quantities should be related by the formulae of Wall et al (3): $r'_1 = K\, r_1$, $r'_2 = r_2/K$, where K is the distribution coefficient in the relation:

$$\frac{[M_1]'}{[M_2]' \text{ (at locus of reaction)}} = \frac{K[M_1]}{[M_2] \text{ (total in reactor)}}$$

The distribution of monomers was measured for water and for soap micelles as possible loci. For water, styrene was measured spectrophotometrically at 2820 A. U. and methyl methacrylate by the interferometer. For micelles, a difference method was used, based upon measurement of monomers added and monomers left undissolved after

coming to equilibrium with soap solution and subsequent centrifuging in a Babcock tube. The undissolved monomers were estimated by volume and refractive index of the recovered layer. The data corresponded to: $K_{water} = 0.02$, $K_{micelles} = 0.7 \pm 0.1$. Similar measurements upon styrene and acrylonitrile yielded: $K_{water} = 0.002$ for high styrene to 0.006 for low styrene mixtures; $K_{micelles} = 0.6 \pm 0.15$.

These results, in view of the correlation formulae, exclude decisively the water phase and the soap micelles as important reaction loci, and the simplest interpretation is that the polymerization occurs in oil phase.

At very low conversions, the picture is shifted, and the product composition tends to resemble that predicted by assuming micelles as the reaction locus; but even at the lowest conversion studied, 0.24 per cent, the resemblance is only partial.

The results reported here can be correlated with the Harkins picture (4) by supposing that the micelles are the earliest reaction locus, but that their micelle character is destroyed as soon as minute amounts of polymer have formed, and that subsequently they behave, with respect to monomer distribution, like oil phase. As polymer dissolved in monomer produces only a small alteration in activity, the tendency toward diffusion equilibrium can result in monomer-polymer particles which duplicate closely the monomer ratio of the oil phase.

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VITA

The author was born in Chicago, Illinois, on January 18, 1915, and received his elementary and secondary education in the public schools of that city. He attended Crane Junior College from 1932 to 1933, and from 1934 to 1936 attended the University of Illinois, from which he received the degree of Bachelor of Science with honors in Chemistry in 1936. He was employed by Standard Oil Company (Indiana) as abstractor and technologist from 1937 to 1941 and during this period also attended University College of the University of Chicago. In 1941 he entered the armed services and served until 1945. In October, 1945, he entered the Graduate College of the University of Illinois. He was employed as a special research assistant under a contract with the Rubber Reserve Corporation from June, 1946, until October, 1947, and held a University fellowship from October, 1947, until May, 1948. He is the author of one previous publication (with Lt. R. M. Silverstein): Sulfonamide Determination in Blood Using Xylenesulfonic Acid as a Protein Precipitant, Journal of Laboratory and Clinical Medicine **29,** 879 (1944).

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